EFFECTS OF LATTICE DEFECTS ON THERMOLUMINESCENCE IN LITHIUM FLUORIDE CRYSTALS

T. G. STOEBE, G. M. GUILMET AND J. K. LEE

Division of Metallurgical Engineering, University of Washington, Seattle, Washington, U.S.A.

The thermoluminescent output of 'pure' LiF single crystals is studied as a function of annealing temperature and cooling rate. The lattice defect structure is characterized using ionic conductivity measurements. The results show that the sensitivity of such crystals to irradiation is highly dependent on prior history; specifically, the intensity of the observed 105 °C thermoluminescence peak depends directly on the concentration of impurity vacany pairs present. The results also show the importance of background impurities in effecting thermoluminescent sensitivity.

INTRODUCTION

The phenomenon of thermoluminescence in LiF crystals is important both for studies of electronic transition processes and for its application in radiation dosimetry. Since the thermoluminescent output of a crystal depends on the freeing of trapped electrons or holes by heating[1], the identity and behavior of the lattice defects which act as the traps can be of major importance in determining the sensitivity and reproducibility of the process. In work using commercial dosimeter crystals, the situation is often complicated by the presence of large amounts of impurities, usually of more than one type, which hinder the identification of the specific defects involved.

All lattice defects[2] in an alkali halide crystal should be able to act as electron or hole traps. This includes cation vacancies, cation impurities, cation vacancy-divalent impurity pairs (dipoles) and complexes, and cation impurity precipitates, as well as similar defects involving the anion lattice, and cation-anion vacancy pairs. Dislocations may also provide trapping centers, probably at charged jogs on the dislocation line[3]. Some of the possible trapping centers due to lattice defect complexes have been discussed by Lidiard[4].

After irradiation by X-rays or gamma-rays, commercial LiF dosimeter crystals usually show six luminescent output peaks during heating between room temperature and 300 °C. Each peak should correspond to a specific lattice defect configuration which acts as the trapping site. While such commercial dosimeter crystals contain a variety of lattice defects, Claffy[5] has shown that the presences of magnesium impurity ions is necessary for the observation of the thermoluminescence peaks observed at about 210° and 285 °C. In this case, Claffy

suggests that these peaks can be identified with Mg^{++}-cation vacancy dipoles and higher order complexes. Claffy also shows that annealing between 100° and 200 °C followed by slow cooling enhances the intensities of the peaks occurring at 105° and 175 °C and nearly eliminates the 210 °C peak. After such a treatment, one would expect the predominent lattice defects in Claffy's doped crystals to be precipitates of the type MgF$_2$. 6LiF and related high order Mg^{++}-cation vacancy complexes[6].

The 105 °C peak has been studied extensively by Grant[7] in Mg-doped crystals. Here, crystals containing 70 and 100 ppm Mg were equilibrated at 300 °C and cooled in air to room temperature. These crystals showed a substantial 105 °C thermoluminescence peak. Crystals which were again annealed before irradiation below 100 °C showed a decrease in the intensity of the 105 °C thermoluminescence peak. Grant also studied dielectric loss, which in such a crystal is caused by Mg^{++}-cation vacancy dipoles, and found a corresponding decay in dielectric loss during these annealing treatments. This leads to the convincing identification of the 105 °C thermoluminescence peak with Mg^{++}-cation vacancy dipoles. This is in apparent contradiction with Claffy's results discussed above.

Grant[7] also showed that higher temperature annealing (at 150 °C) prior to irradiation caused a decrease in the number of Mg^{++}-cation vacancy dipoles as recorded by dielectric loss; however, the intensity of the 105 °C thermoluminescent peak increased. This was explained by postulating that a recombination center must be located nearby to cause thermoluminescent emission. The 210 °C glow peak disappears during such an annealing treatment, which means that recombination centers

189

which had been tied up in the 210 °C peak could now be available in solution. With more recombination centers available, a higher fraction of the dipoles can contribute to the thermoluminescent output. Thus, even though the concentration of these pairs decreases, an increased probability for a thermoluminescent transition can result.

A number of problems remain unresolved concerning the identity of the lattice defects responsible for the overall thermoluminescence spectrum. Even in crystals with an overwhelming concentration of impurity-vacancy pairs, the 105 °C peak is not the major peak. Higher order impurity-vacancy complexes could indeed play a role, but no consistent picture has been presented. It is also known that the annealing temperature and cooling rate should play a role, but much of the work on this subject has been emperical. The greatest problem is probably the uncertainty connected with unknown and undetermined impurity species and contents in the crystals employed in much of the research in this field; many researchers have ignored the explicit influence of impurities or even of lattice defects on the sensitivity of their dosimeter crystals to irradiation.

In this paper, the effects on the thermoluminescent sensitivity caused by different defect structures, as produced by different annealing treatments, is investigated in three different sets of 'pure' LiF crystals. The equilibrium lattice defect structure, as characterized by ionic conductivity measurements, is used to explore the effects of background impurities on the thermoluminescent behavior and to investigate the effects of heat treatments on the thermoluminescence output directly.

EXPERIMENTAL PROCEDURE

Single crystal specimens of dimensions 5 mm by 5 mm by 1 mm thick were prepared by cleavage from three single crystal boules of 'pure' LiF supplied by the Harshaw Chemical Company; crystals from these boules are labeled as set I, set II, and set III.

The specimens were polished to 0.5 mm thickness for optimum thermoluminescent readout, and were standarized by annealing for one hour at 500 °C, followed by furnace cooling to 100 °C, and were then annealed at that temperature for 24 hours. The standardized specimens were exposed to an X-ray dose of 100 R and the thermoluminescent curve for each was determined on a commercial TLD reader within one hour of irradiation. The
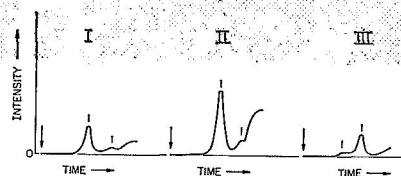

FIG. 1. Thermoluminescent output for typical samples from sets I, II and III. Peak temperatures are indicated at 105 °C and 210 °C, determined from a time-temperature calibration of the output of the TLD reader. The third peak in each case is due to surface states (triboluminescence).

thermoluminescence curve is read in about 30 seconds, and does not effect the existing defect state of the crystal.

From each set of specimens from each boule, twelve specimens with nearly identical peak heights, as normalized by sample weight, were chosen for the remaining experiments. Typical calibration curves for samples from each of the original single crystal boules are shown in Figure 1 for each set, and are used further as reference curves.

The same samples were then annealed for one hour at specified temperatures between 200° and 700 °C. The samples were either air cooled (average cooling rate about 50 °C/min) or furnace cooled (average cooling rate 2 °C/min) to room temperature, after which the thermoluminescent output was determined again. Ionic conductivity experiments were performed on two samples from each set; the A.C. conductivity was determined on heating at 1 °C/min between 200 aud 650 °C using a Wayne–Kerr A.C. Bridge.

EXPERIMENTAL RESULTS

The thermoluminescent glow peaks shown for each set in Figure 1 indicate a strong 105 °C peak and a weak 210 °C peak in sets I and II. Set III shows only an indication of a 105 °C peak and a stronger high temperature peak, often at a temperature less than 210 °C. The third peak in all cases is triboluminescence due to surface trapping states, which varies in intensity from sample to sample and is unimportant in the present case.

The ionic conductivity results for typical samples of each set are shown in Figure 2. These curves show the normal high temperature intrinsic region and an extrinsic region at lower temperatures due to the presence of divalent impurities. The downward curvature observed at the low temperature end in set III indicates the onset of the association of cation vacancies and divalent impurities into
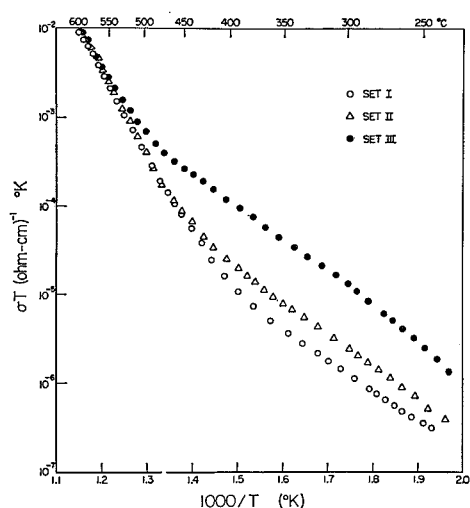
FIG. 2. Ionic conductivity plot for typical specimens from sets I, II and III. Data derived from this plot are given in Table I.
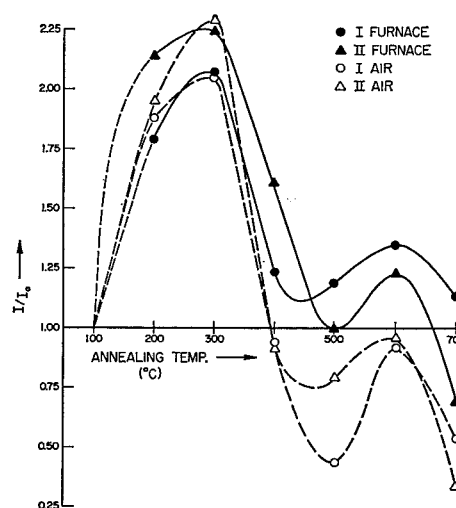

FIG. 3. Thermoluminescent intensity for sets I and II after the indicated annealing and cooling treatments, reported as the fractional change compared with the reference sample.

dipoles. In all of these samples these impurity-vacancy dipoles should be the predominant equilibrium defect between about 100° and 200 °C; below 100 °C, trimers (groups of three such pairs) should be predominant. In these pure crystals it is doubtful if actual precipitates would form, except perhaps after long time storage at room temperature.

Using the extrapolated knee temperature and the data of Stoebe and Pratt[8] for the intrinsic vacancy concentration, the divalent impurity concentrations may be determined for these crystals. These are shown in Table I along with the knee temperature and the activation energy determined from the slope in the extrinsic region.

TABLE I

Data determined from ionic conduction results

	Knee temp, °C	Divalent ion concentration, ppm	Activation energy in extrinsic region, eV
Set I	425	0.21	0.68±0.02
Set II	449	0.37	0.69±0.02
Set III	516	2.5	0.70±0.02

The slope of the extrinsic region indicates the motion energy of cation vacancies in LiF, and agrees well with other recent results[8,9]. The

shape of the extrinsic region of the conductivity plot indicates that the crystals are free of OH⁻ impurity ions[10].

The intensities of the 105 °C peak after annealing and cooling either in air or in the furnace for samples in sets I and II are shown in Figure 3. The fractional change due to the annealing treatment is shown, where the change is compared to the intensity of the 105 °C peak shown in the reference curve for that sample. Two peaks in the output are seen here, one for annealing at about 300 °C and the other for annealing at 600 °C. These annealing treatments had very little effect on the intensity of the 210 °C peak.

DISCUSSION OF RESULTS

The ionic conductivity results shown in Figure 2 and Table I indicate that the crystals used in these experiments are quite pure as far as polyvalent cations are concerned, with the purity increasing from set III to set I. Since the reference samples were standarized by heating at 100 °C for 24 hours, the ionic conduction results indicate that the predominant defect in these standarized crystals should be trimers, but with dipoles present in a significant concentration.

From Grant's work, one expects the 150 °C peak to be due to dipoles; from the conductivity results, one expects the dipole concentration to increase between sets I, II and III. However, the thermo-

luminescence in the reference samples (Figure 1) does not show this. The intensity of this peak does increase from set I to set II, but the peak is very small in set III. In fact, none of the results for set III are consistant with the other observations. Since this sample has the lowest purity, it is possible that it contains different impurities than the other two sets, which may lead to complications. A detailed analysis is necessary to clarify this point, and set III will therefore not be discussed further. The results for sets I and II are explained in a simple manner as being due to a divalent impurity such as Mg^{++} in the crystals.

The annealing studies show a large increase in the intensity of the 110 °C peak after annealing at 200° and 300 °C in the air-cooled crystals, and at 200°, 300° and 400 °C in the furnace-cooled crystals. This is due to an increase in the dipole concentration over that in the reference samples. The air-cooled samples pass rapidly from the region of free vacancies and impurities through the dipole region but the cooling rate is not fast enough to avoid the formation of dipoles. Upon furnace cooling, the formation of dipoles during cooling is even more effective.

Annealing and quenching from higher temperatures produces a quenched-in structure consisting of more free vacancies and isolated impurities and consequently fewer dipoles. Consequently, Figure 3 shows that fewer dipoles are present in the air-cooled crystals than in the reference samples at all annealing temperatures above 400 °C in the air-cooled crystals. Crystals quenched from temperatures well above the knee of the conductivity curves contain an even greater concentration of (intrinsic) vacancies and hence a greater probability of forming dipoles during the quench. This is observed in Figure 3 as an increase in thermoluminescent output of crystals cooled from above 500 °C. Quenching from the highest temperature (700 °C) could lead to the formation of dipole-vacancy complexes and vacancy precipitates; consequently it is conceivable that the peak observed at 600 °C indicates the optimum quenching temperature for the formation of dipoles during the quench from the intrinsic region.

Figure 3 shows that the furnace cooled samples exhibit the same general behavior as air cooled samples. However, there are always more dipoles in the furnace cooled samples after cooling from high temperatures than in the reference samples, as expected from the much slower cooling rate.

The changes in the thermoluminescent intensities for the 105 °C peak after the annealing treatments may not, of course, be entirely due to changes in the dipole concentration. It may also be due to changes in the concentration of recombination centers, as discussed earlier. If these recombination centers are cation or anion vacancies, similar influences on the intensities may be expected as are discussed above.

SUMMARY AND CONCLUSIONS

The results obtained show that the thermoluminescent sensitivity of 'pure' LiF crystals is highly dependent upon prior treatment, and the observed dependence can be explained in terms of the behavior of divalent impurity-vacancy dipoles in the crystal. Several of the details of the annealing behavior need further clarification, including the effect of cooling from the highest temperature of anneal.

The results emphasize the importance and usefulness of characterizing the lattice defect structure of such crystals by using ionic conductivity measurements; dielectric loss and optical absorption measurements would also be useful for defect structure analysis.

These studies also show the importance of background impurities in thermoluminescent behavior. The inconsistent results in set III were attributed to this, and the impurity levels determined for sets I and II are in the 'background' region. Any sort of chemical or spectrographic analysis would have difficulties in determining the background impurity contents of these crystals. Knowledge of the influence of small amounts of impurities in affecting thermoluminescent will be very useful for future studies of the effects of impurity ions on thermoluminescence.

ACKNOWLEDGEMENTS

REFERENCES

1. See, for example, J. H. Schulman, in *Luminescence Dosimetry*, USAEC, 1967, p. 3.
2. See. for example, F. A. Kröger, *Chemistry of Imperfect Crystals*, North–Holland, Amsterdam, 1964.
3. R. W. Whitworth, *Phil. Mag.*, **17**, 1207 (1968).
4. A. B. Lidiard, *J. Appl. Phys.*, **33**, 414 (1962).
5. E. W. Claffy, in *Luminescence Dosimetry*, p. 74.
6. E. Barsis, E. Lilley and A. Taylor, *Proc. Brit. Ceram. Soc.*, **9**, (1967); E. Lilley, private communication.
7. R. M. Grant, Ph.D. Thesis, University of Wisconsin, 1965; R. M. Grant and J. R. Cameron, *J. Appl. Phys.*, **37**, 3791 (1966).
8. T. G. Stoebe and P. L. Pratt, *Proc. Brit. Ceram. Soc.*, **9**, 181 (1967).
9. S. C. Jain and G. D. Sootha, *Phys. Stat. Sol.*, **22**, 505 (1967).
10. T. G. Stoebe, *J. Phys. Chem. Solids*, **28**, 1375 (1967).

DISCUSSION

Question (P. C. MEHENDRU)   How does the sensitivity of LiF phosphor suffer on repeated using?

Reply   If heat treated once again it does not suffer at all.

Question   How is the energy response of these phosphors?

Reply   Fairly linear as far as γ- and X-ray are concerned.

Question   What is the maximum amount of dosage which human body can receive safely? What is the minimum dosage these phosphors can easily detect?

Reply   About 10 mr can be easily measured.